US6110616 describes copolymers of butadiene and styrene and their subsequent sulphonation to prepare cation-exchange membranes for fuel cells.

A further class of partially fluorinated cation-exchange membranes can be prepared by radiation grafting and subsequent sulphonation. Here, as described in EP667983 or DE19844645, a grafting reaction, preferably with styrene, is carried out on a previously irradiated polymer film. In a subsequent sulphonation reaction, the side chains are then sulphonated. Crosslinking can also carried out simultaneously with the grafting reaction so as to alter the mechanical properties.
Apart from the above membranes, a further class of unfluorinated membranes obtained by sulphonation of high-temperature-stable thermoplastics has been developed. Thus, membranes made of sulphonated polyether ketones (DE4219077, EP96/01177), sulphonated polysulphone (J. Membr. Sci. 83 (1993) p.211) or sulphonated polyphenylene sulphide (DE19527435) are known.
Ionomers prepared from sulphonated polyether ketones are described in WO 00/15691.

Also known are acid-based blend membranes which, as described in DE19817374 or WO 01/18894, are prepared by mixing sulphonated polymers and basic polymers. In addition the application WO 99/101165 describes membranes made from polymers containing sulphonic acid groups.

To improve the membrane properties further, a cation-exchange membrane known from the prior art can be mixed with a high-temperature-stable polymer. The preparation and properties of cation-exchange membranes comprising blends of sulphonated PEK and a) polysulphones (DE4422158), b) aromatic polyamides (42445264) or c) polybenzimidazole (DE19851498) have been described.

A disadvantage of all these cation-exchange membranes is the fact that the membrane has to be moistened, the operating temperature is restricted to 100°C and the membranes have a high methanol permeability. The reason for these disadvantages is the conductivity mechanism of the membrane in which the transport of protons is coupled with the transport of the water molecule. This is referred to as the "vehicle mechanism" (K.-D. Kreuer, Chem. Mater. 1996, 8, 610-641).

As a second category, polymer electrolyte membranes comprising complexes of basic polymers and strong acids have been developed. Thus describe

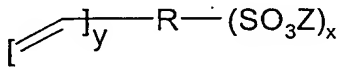
Claims

1. Proton-conducting polymer membrane which is based on polyvinylsulphonic acid and is obtainable by a process comprising the steps
   A) mixing of a polymer with vinyl-containing sulphonic acid,
   B) formation of a flat structure using the mixture from step A) on a support,
   C) polymerization of the vinyl-containing sulphonic acid present in the flat structure from step B),
   characterized in that the membrane has an intrinsic conductivity of at least 0.001 S/cm.

2. Membrane according to Claim 1, characterized in that the polymer used in step A) is a high-temperature-stable polymer containing at least one nitrogen, oxygen and/or sulphur atom in one repeating unit or in different repeating units.

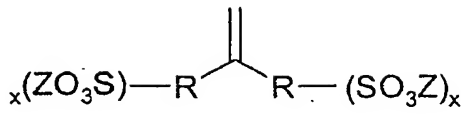
3. Membrane according to Claim 1, characterized in that one or more polyazoles and/or polysulphones are used in step A).

4. Membrane according to Claim 1, characterized in that the mixture prepared in step A) contains compounds of the formula



where
R is a bond, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, COOZ, -CN, NZ_2,
the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, -CN, and
x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,
y is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or the formula



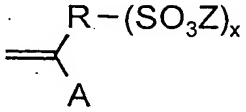
where

R is a bond, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or the formula



where

A is a group of the formula $COOR^2$, CN, $CONR^2_2$, OR^2 and/or R^2, where R^2 is hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn subtituted by halogen, -OH, COOZ, -CN, NZ_2,

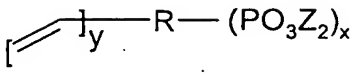
R is a bond, a divalent C1-C15-alkylene group, divalent C1-C15-alkylenoxy group, for example ethylenoxy group, or divalent C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

5. Membrane according to Claim 1, characterized in that the mixture prepared in step A) comprises vinyl-containing phosphonic acid.

6. Membrane according to Claim 5, characterized in that the mixture prepared in step A) contains compounds of the formula



where

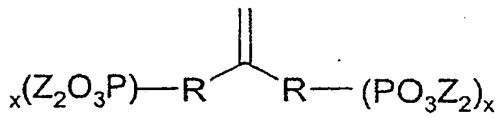
R is a bond, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

y is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or the formula



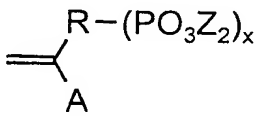
where

R is a bond, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10,

and/or the formula



where

A is a group of the formula $COOR^2$, CN, $CONR^2_2$, OR^2 and/or R^2, where R^2 is hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn subtituted by halogen, -OH, COOZ, -CN, NZ_2,

R is a bond, a divalent C1-C15-alkylene group, divalent C1-C15-alkylenoxy group, for example ethylenoxy group, or divalent C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, COOZ, -CN, NZ_2,

the radicals Z are each, independently of one another, hydrogen, a C1-C15-alkyl group, C1-C15-alkoxy group, ethylenoxy group or C5-C20-aryl or heteroaryl group, with the above radicals being able to be in turn substituted by halogen, -OH, -CN, and

x is 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10.

7. Membrane according to Claim 5 or 6, characterized in that the weight ratio of vinyl-containing phosphonic acid to vinyl-containing sulphonic acid is in the range from 1:100 to 99:1.

8. Membrane according to Claim 1, characterized in that the mixture prepared in step A) contains monomers capable of crosslinking.

9. Membrane according to Claim 1, characterized in that the polymerization in step C) is effected by means of a substance which is capable of forming free radicals.

10. Membrane according to Claim 1, characterized in that the polymerization in step C) is carried out by irradiation with IR or NIR Light, UV light, β-rays, γ-rays and/or electron beams.

11. Membrane according to Claim 1, characterized in that the membrane comprises from 1 to 90% by weight of the polymer and from 99 to 0.5% by weight of polyvinylsulphonic acid.

12. Membrane according to Claim 1, characterized in that the membrane has a layer comprising a catalytically active component.

13. Mixture comprising vinyl-containing sulphonic acid as defined in Claim 4, and at least one polymer which has a solubility of at least 1% by weight in the vinyl-containing sulphonic acid.

14. Mixture according to Claim 13, characterized in that the polymer used contains at least one nitrogen, oxygen and/or sulphur atom in one repeating unit or in different repeating units.

15. Mixture according to Claim 13, characterized in that it contains at least one monomer capable of crosslinking.

16. Mixture according to Claim 13, characterized in that it contains at least one initiator which is capable of forming free radicals.

17. Mixture according to Claim 13, characterized in that the mixture comprises at least one vinyl-containing phosphonic acid.

18. Membrane-electrode unit containing at least one membrane according to one or more of Claims 1 to 12.

19. Fuel cell containing one or more membrane-electrode units according to Claim 18 and/or one of more membranes according to any of Claims 1 to 12.